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**"Modeling of Carbon Monoxide Oxidation Kinetics
Over NASA Carbon Dioxide Laser Catalysts"**

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Submitted by

**Richard K. Herz
Chemical Engineering Group, Mail Code B-010
Department of Applied Mechanics and Engineering Sciences
University of California at San Diego
La Jolla, CA 92093**

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INTRODUCTION

Oxidation of CO to CO₂ is an important reaction technologically and environmentally, and a complex and interesting reaction scientifically. In most cases, the reaction is carried out in order to remove CO as an environmental hazard. A major application of heterogeneous catalysts is catalytic oxidation of CO in the exhaust of combustion devices. The reaction over catalysts in exhaust gas is fast and often mass-transfer-limited since exhaust gases are hot and O₂/CO ratios are high. The main challenges to catalyst designers are to control thermal sintering and chemical poisoning of the active materials.

In the application addressed in this project, sealed CO₂ lasers, CO oxidation is carried out in order to recombine CO and O₂ formed by dissociation of CO₂ in the laser discharge zone. This application differs from exhaust clean-up in ways that present completely different challenges to designers of CO oxidation catalysts. Gas temperatures in lasers must be held low, in the range 0°C ± 40°C, in order to minimize power consumption and to keep the gas cool in the laser discharge volume. O₂/CO ratios are stoichiometric or less since these species are formed by CO₂ dissociation and some oxygen may be consumed in other reactions. Additional O₂ cannot be added to facilitate CO oxidation because the laser discharge is degraded by O₂.

Conventional catalysts are not active at low temperatures and low O₂/CO ratios. Over conventional noble-metal catalysts, CO and O₂ compete for the same adsorption sites on the metal surface. At low temperatures and low O₂/CO ratios, adsorbed CO blankets the active surface of the noble metal and prevents O₂ adsorption and reaction. Over conventional base-metal-oxide catalysts, oxygen is held too strongly to for it to be removed by CO at low temperatures.

Currently, Pt/SnO₂ and related materials are the most promising catalysts for use in sealed CO₂ lasers. Stark and Harris [1] reported significant reaction rates over Pt/SnO₂ and Pd/SnO₂ at temperatures as low as -27°C, conditions under which conventional catalysts are inactive.

When Pt and Pd are used in conventional noble-metal CO oxidation catalysts, they are usually dispersed over Al₂O₃. Al₂O₃ does not participate in CO oxidation and serves as an inert support that maintains high noble-metal dispersions. CO adsorbed on the noble metal strongly inhibits O₂ adsorption and, thus, the reaction. In contrast, Bond and coworkers [2,3] demonstrated that SnO₂ interacts synergistically with the noble metal to produce a catalytic activity that is substantially higher than either component separately. Since CO and O₂ have to compete for the same surface sites over noble metals, it is likely that the mixture of the two components in the composite NMRO material provides separate sites for CO and O₂ adsorption: CO adsorbed on the metal can react with oxygen held by the SnO₂. While this hypothesis is probably part of the full explanation, experimental evidence for Pt-Sn metal alloy formation [4] and the sensitivity of the catalysts to H₂O [5,76], suggest that much remains to be learned about low temperature CO oxidation over Pt/SnO₂ and related materials. How Pt/SnO₂ works and how more active and stable materials can be synthesized remain open questions.

David Schryer at NASA's Langley Research Center coined the phrase "noble-metal reducible-oxide" and acronym "NMRO" to refer to Pt/SnO₂ and related materials. The terms highlight the ease with which SnO₂ can be reduced by CO and H₂ relative to refractory oxides such as Al₂O₃. As intended by this author, Schryer, and coworkers, the class of NMRO materials includes a wide range of materials in applications beyond sealed CO₂ lasers. The class typically consists of a zero-valent metal dispersed over or inter-mixed with a metal oxide that can be reduced to some extent under reaction or pretreatment conditions. Depending on conditions, any of the Group VIIIA and IB elements may serve as the "noble metal." The class also includes materials in which the noble metal is oxidized under some conditions, materials in which the some of the metal oxide may become completely reduced to the parent metal under some conditions, and complex materials composed of more than a single metal and a single oxide.

NMRO materials often exhibit "strong metal-support interactions," or "SMSI" behavior, using terminology introduced in the late 1970's by Tauster and coworkers [6, 7]. They applied the term SMSI to refer to behavior exhibited by Pt-group metals dispersed over TiO_2 following high temperature reduction in H_2 . Subsequent work, which was reviewed by Vannice at the NASA/RSRE CO_2 Laser Conference in 1986 [8], has shown that SMSI behavior is due to interaction of partially reduced titania (" TiO_x ") species interacting with the noble metal. Thus, TiO_2 is a "reducible oxide" and Pt/TiO_2 and Rh/TiO_2 are NMRO materials. Relative to SMSI, the acronym NMRO is more specific in the sense that it refers to interactions only between zero-valent metals and reducible oxides and not between metals and other types of supports. Relative to SMSI, the acronym NMRO is more general in the sense that it refers to a material itself rather than a particular behavior of the material. The term NMRO is also more general in the sense that it includes systems where the reducible oxide does not "support" the metal, for example, materials with high metal-oxide ratios in bulk form or dispersed over an inert support.

NMRO materials have many important applications, as the examples in Tables 1 through 11 demonstrate. Many of the applications involve oxidation or reduction reactions which involve transfer of oxygen atoms. In a noncatalytic application, Pt/SnO_2 and other materials serve as gas detectors (Table 1). Reducing gases such as CO chemisorb on the metal, reduce the oxide in a stoichiometric reaction, and change the electrical characteristics of the oxide, providing the sensor signal. NMRO materials catalyze CO oxidation in many types of applications (Table 2), and CO, H_2 and hydrocarbon oxidation and NO reduction in automotive "three-way" catalysts (Table 3). Hydrocarbons can be completely oxidized in catalytic heaters (Table 4) or partially oxidized over NMRO materials (Table 5). CO_2 and CO can be hydrogenated over NMRO catalysts to form methane and higher hydrocarbons in Fischer-Tropsch processes (Tables 6 and 7). Methanol and other oxygenated products can also be formed during CO hydrogenation (Table 8). In reactions not involving oxygen transfer, NMRO materials catalyze reforming reactions of hydrocarbons (Table 9). NMRO materials also serve as catalytic electrodes in electrochemical processes and catalyze photochemical processes (Table 10). Miscellaneous applications are listed in Table 11.

An essential aspect of NMRO materials of interest here is that the combination of noble metal and reducible oxide has a synergistic effect: these composite materials show unique catalytic activity which is not a simple addition of the characteristics of the separate materials. Synergistic effects have been demonstrated over Pt/SnO_2 CO oxidation catalysts [2,3], Ag/MnO_2 CO oxidation catalysts [9], Pt/TiO_2 [10] and Rh/TiO_2 [11] CO hydrogenation catalysts, and for NO reduction [12] and ethylene hydrogenation [3] catalysts, for example.

There are three general ways in which the two types of components in NMRO composite materials can interact synergistically:

- (a) one component may alter the properties of the other component,
- (b) the two components may each provide independent catalytic functions in a complex reaction mechanism,
- (c) unique catalytic sites may be formed through combination of the two components at the atomic level.

All three of these interactions may be important in low temperature CO oxidation over NMRO catalysts.

In order to organize the material in this review, the effect of the noble metal on the oxide will be discussed first, followed by the effect of the oxide on the noble metal, the interaction of the

noble metal and oxide to form unique catalytic sites, and the possible ways in which the CO oxidation reaction is catalyzed by the NMRO materials.

METAL EFFECT ON OXIDE

Metals dispersed over metal oxides have been shown to catalyze the reduction of the oxide by CO and H₂: Ru catalyzed reduction of Fe oxide [13], reduction of SnO₂ catalyzed by various metals [2,14], Pt catalyzed reduction of various metal oxides [15-17], Pd catalyzed reduction of various oxides [16], and Rh catalyzed reduction of TiO₂ [18]. In some cases, interaction with the noble metal can stabilize reduced oxide species against reoxidation [17]. In other cases, the reoxidation of the reducible oxide can be catalyzed, for example, Pd catalyzed oxidation of SnO₂ [2]. For H₂ and O₂, at least one function of the metal in catalyzing oxide reduction involves catalyzing dissociation of the diatomic molecules during their dissociative adsorption. For adsorbed CO, H, and O on the metal, the oxidation and reduction reactions may occur at the interface between the metal and the oxide. Defect sites in the oxide located at the metal-oxide interface may participate in the reaction, for example, oxygen vacancies at the interface between Pt and ceria [19]. Alternatively, adsorbed CO, H and O may "spillover" from the metal and move out over the surface of the reducible oxide. Bond, et al. [3,2] proposed that the synergistic enhancement of CO oxidation over Pd/SnO₂ is due to spillover of both CO and O from the Pd onto the SnO₂, with reoxidation of the support being the slow step in the reaction. Studies of H spillover include: Pt/SnO₂ [20], Pt/TiO₂ [21,22], Pt/ReO_x/Al₂O₃ [23], and Rh/Al₂O₃ [24].

OXIDE EFFECT ON METAL

The effects of the oxide on the metal are more varied. Choice of the metal oxide affects the dispersion of the reduced metal that can be achieved, for example, for Pd/SnO₂ [2] and Ru [25]. The dispersion and distribution of metals between metal particles in bimetallic catalysts can also be affected by the support, for example, for Rh/Au catalysts [26]. These effects indicate that there can be significant interactions between the metal and the oxide support.

Except for gold, all of the "noble" metals can be oxidized to some extent under some conditions - pretreatment conditions if not reaction conditions - even supported Pt [27]. Oxide supports tend to stabilize the oxidized form of supported noble and base metals against reduction treatments, for example, for Cu in Cu/ZnO [28-29], Pt on Al₂O₃ [30], Pt on SnO₂ [31], Pd on SnO₂ [32], Ni on MgO/SiO₂ [33]. Oxidation of large supported metal particles to form an oxide that "wets" the supporting oxide, followed by re-reduction of the noble metal, can lead to redistribution of the supported metal, [30]. Under severe oxidizing conditions, compound formation can occur between the oxide form of the supported metal and the oxide support, deactivating the metal [34].

For small, oxide-supported metal particles, the electronic structure of the metal atoms may be affected by the oxide, affecting the metal's catalytic activity. Doi and coworkers [25,35] found the electronic structure of Ru atoms in CO hydrogenation to be markedly affected by metal oxide supports: Ru atoms on basic oxides like MgO and TiO₂ were electron rich but those on acidic oxides such as silica-alumina and titania-alumina were electron deficient, affecting the yield of hydrocarbons. In some cases, different phases of the reducible oxide interact with the noble metal differently. Wolf and coworkers [36] compared Pt on the rutile and anatase phases of TiO₂ and found that CO adsorbed linearly on Pt on anatase and in the bridged mode on Pt on rutile, with the Pt/rutile being more active for CO oxidation. SnO₂ was determined to not be a direct catalyst but to modify supported Pt and Pd in studies of electrochemical oxidation of methanol [37-39].

A major complication in analyzing such evidence of synergistic behavior over NMRO materials is that the structure and composition of these composite materials can be quite heterogeneous at the atomic level. This heterogeneity can be caused by a number of mechanisms, and experimental determination of surface structure and composition at the atomic level is extraordinarily difficult. Until this stage in the review, one may have inferred that the materials are composed of metal particles in contact with a reducible oxide support, each component modifying the other to some extent. This picture is accurate for some materials under some conditions. However, direct intermixing of various forms of the two components can occur at the atomic level, especially under reducing conditions. Under reducing conditions, the reducible oxide may be reduced to the extent that suboxide species can diffuse into the metal or reduced completely such that the parent metal of the oxide forms a metal alloy with the noble metal. This complexity is a focus of the rest of this section and the next section.

Oxide or suboxide species can partially or completely cover the surfaces of supported metal particles, as has been shown for Pt/TiO₂ [62]. There are several possible mechanisms for this "decoration" of supported metal particles by oxide species. One mechanism can be a gradual growth of the oxide over the surface on the metal particle, or "encapsulation," that is driven by interfacial energies [40,41]. Another mechanism involves dissolution of suboxide species in the metal under reducing conditions, followed by segregation to the surface of the metal under oxidizing conditions, as Gorte [42] showed for Pt/TiO₂ and Pt/Nb₂O₅ and Tang et al. [43] showed for Pt/TiO₂. Under severe reducing conditions, the oxide may be reduced to the metal and form an alloy with the supported noble metal [4]. Under subsequent oxidizing conditions, segregation may occur to produce oxide species on the surface of the noble metal or redistribute the noble metal over the surface of the oxide.

Once decoration of the metal with oxide species occurs, the oxide species can affect catalytic activity by serving as an inert agent that blocks and deactivates sites on the metal or by modifying the electronic structure and catalytic properties of neighboring noble metal atoms. White and coworkers [44,45] found that TiO_x on Rh both blocks CO adsorption by covering some Rh sites and modifies CO adsorption on other Rh sites. In a calorimetric study of CO and H adsorption over Pt on the anatase phase of TiO₂, Herrmann, et al. [46] found that the reduced support modifies the chemical properties of the surface Pt atoms. Sadeghi and Henrich [47] found evidence for charge transfer from reduced Ti cations to Rh atoms in Rh/TiO₂.

FORMATION OF UNIQUE SITES

Alloy formation between the noble metal and the parent metal of the reducible oxide can form unique catalytic sites, either through modification of the alloyed noble metal atoms or formation of sites involving both types of metal atoms. In previous work [4,159], Hoflund and coworkers provided evidence for Pt-Sn alloy formation in Pt/SnO₂ catalysts. Pt-Sn alloys as well as Sn-aluminates and SnO have been found in Pt/Sn/Al₂O₃ hydrocarbon reforming catalysts [48]. McCabe and Mitchell [66,67] demonstrated synergistic CO oxidation activity with Pt-Ag alloys, and Oh and Carpenter [68] did so for Pt-Rh alloys.

Unique catalytic sites may also form at the interface between the noble metal and its oxide support and between the metal and partial overlayers of oxide or suboxide on the metal. TiO_x overlayers have been proposed to catalyze the dissociation of CO during CO hydrogenation to methane and higher hydrocarbons for Pt [42,43, 45,47,49-52] and Rh [45,50,53,54]. One model is that the oxygen end of CO is attracted to the oxide, weakening the bond between the oxygen end and the carbon end bonded to the metal [8]. The interaction between TiO_x overlayers and Pd catalyzes the formation of methanol during CO hydrogenation [55].

FUNDAMENTAL STUDIES OF NMRO MATERIALS

Because of the complex interactions possible in NMRO materials, interactions which give them their unique synergistic properties, a wide variety of experimental techniques are required to analyze the materials and their properties. Surface sensitive techniques, such as those used in references [31,47,56-58] that can be used to probe the surface composition and structure of the materials are necessary, in addition to kinetic measurements. Although porous, high-surface-area catalysts are desired in applications, "model" systems composed of one component distributed over the flat surface plane of a large single crystal of the other component are often preferable for fundamental studies [10,42,59-61].

CO OXIDATION AND NMRO CATALYSTS

During oxidation of CO by O₂, whether in the gas-phase or over a catalyst surface, two basic steps must occur: dissociation of the O₂ molecule and formation of an O-CO bond. These two steps usually occur in separate events. Over the surface of a catalyst, then, O₂ must adsorb and dissociate and CO must adsorb next to and react with an O atom [63].

Over zero-valent noble metals (on inert, nonreducible-oxide supports), CO and O₂ compete for the same sites on the surface. Low temperature activity is minimal because CO covers the metal surface and inhibits O₂ adsorption. CO dominates the surface because O₂ adsorption has more stringent open site requirements since it must dissociate and because O₂ adsorption probabilities or "sticking coefficients" on bare metal surfaces are at least an order of magnitude lower than CO sticking coefficients [64,65].

Over metal oxide surfaces the picture is more complex. However, low temperature CO oxidation activity is also minimal over simple oxide surfaces, primarily because of the strong bonding of oxygen to the surface [63].

NMRO materials such as Pt/SnO₂ are synergistic composite materials with significant low temperature CO oxidation activity. The limiting steps with conventional catalysts involve oxygen: competition between O₂ and CO adsorption over metal catalysts and removal of oxygen bound to oxide catalysts. Thus, we can postulate that one or both of these processes are facilitated over NMRO catalysts: O₂ adsorption and dissociation is enhanced relative to CO adsorption and/or oxygen can be removed from the oxide surface relatively easily. Evidence that competition between CO and O₂ is reduced over NMRO materials comes from kinetic studies that show that CO doesn't inhibit the reaction significantly, as it does over noble metals supported on non-reducible, inert supports [71,77,78].

An obvious way that the first process, O₂ adsorption and dissociation, can be enhanced relative to CO adsorption is provision of separate but neighboring sites for the two molecules. Hoflund and coworkers [4, 159] showed that a Pt-Sn metal alloy can form in Pt/SnO₂ during reducing pretreatments and NASA Langley researchers [76] showed that a reducing pretreatment is required to obtain high activity over Pt/SnO₂. If a Pt-Sn alloy were stable during low temperature CO oxidation, competition between CO and O₂ could be reduced if CO adsorbed on Pt atoms and O₂ adsorbed on Sn atoms or a site consisting of a Pt and an Sn atom. Such a scenario is similar to the explanations proposed by McCabe and Mitchell [66,67] to explain enhanced CO oxidation activity over Pt/Ag/Al₂O₃ and by Oh and Carpenter [68] for enhanced CO oxidation activity over Pt/Rh/Al₂O₃.

The second process mentioned above is that CO adsorbs on noble metal atoms and then removes oxygen from neighboring regions of reducible oxide. Wolf [36,72] and coworkers proposed that O transfer from the rutile form of TiO₂ participates in CO oxidation over Pt/TiO₂ as

well as the usual Langmuir-Hinshelwood mechanism over Pt. Jun, et al. [73] found that O chemisorbed on Ag/SnO₂ participated in the complete oxidation of ethylene and lowered the selectivity for ethylene oxide.

Both of the processes just discussed involve reaction at atomic interfaces between the two components of the composite materials. In either case, the preparation and pretreatment of the catalyst to obtain intimate contact between the noble metal and the reducible oxide becomes critical. Further work is required to determine the importance, in determining this atomic or interfacial contact, of alloy formation between the noble metal and the parent metal of the reducible oxide (e.g., Pt-Sn alloy formation) and the importance of suboxide species on noble metal surfaces. In addition to catalyst preparation and activity testing, fundamental studies of the solid state thermodynamics and kinetics of NMRO materials are required.

A third possibility is that one of the components serves as a reservoir, or "port hole" in the terminology of Boudart and H. S. Taylor [160], which supplies one of the reactants to the other component. Bond and coworkers [2,3] proposed that spillover of both CO and O from noble metal to the oxide is important in low temperature SnO₂-based NMRO catalysts. A different scenario was proposed by Imamura, et al. [9] to explain low temperature CO oxidation over Ag/MnO₂. They proposed that the role of MnO₂ is to serve as a readily re-oxidizable reservoir of O that keeps Ag supplied with O and in an oxidized state. They further proposed that CO was oxidized by reaction with the Ag oxide. One might call this proposal "reverse" spillover from the oxide support to the metal.

In addition to eliminating competition between CO and O₂ by the presence of separate adsorption sites, O₂ dissociation may be facilitated over NMRO catalysts. Booker and Keiser [70] showed that surface hydroxyl groups on Rh/Al₂O₃ can oxidize adsorbed CO to CO₂. Croft and Fuller [5] showed that the presence of gas-phase H₂O can enhance the activity of Pd/SnO₂. Studies by Schryer and coworkers at NASA Langley [76] have shown that the presence of H₂O can affect the behavior of Pt/SnO₂ catalysts. The way in which H₂O might participate is suggested by the mechanism of homogeneous CO oxidation in the gas phase [63,69]. In the gas phase, traces of H₂ or H₂O serve as a catalyst of the CO oxidation reaction. O₂ is dissociated by collision with H to form OH and O radicals. CO is oxidized by collision with OH radicals to form CO₂ and H, not by collision with O atoms. Oxide surfaces are usually found in a hydroxylated and protonated state, even when H₂O has not been added to a reactant stream deliberately [32,74,75, 161]. Hoflund and coworkers obtained evidence for the presence of hydroxyl groups on Pt/SnO₂ [159]. Hydroxyl groups and protons on the reducible-oxide surface might participate by catalyzing the dissociation of O₂. Finally, the possibility that CO is oxidized over NMRO catalysts by surface hydroxyl groups, as in the homogeneous reaction mechanism, must also be considered. A complete kinetic model for CO oxidation over Pt/SnO₂ involving water and hydroxyl groups is presented elsewhere [76].

Determining which of the processes proposed above - or an entirely unexpected process - oxidizes CO at low temperatures over NMRO materials will take further careful work. Some of the recent work involving Au catalysts keeps the work stimulating. Over Au co-precipitated with a variety of base metal oxides, Haruta, et al. [79] obtained complete oxidation of 1% CO in air at -70°C (66 cm³/min over 0.2 g). Huber, et al. [80] observed reaction between CO and O₂ in a matrix with Au at 4 K.

PUBLICATIONS RESULTING FROM THIS GRANT

1. Herz, R. K., "CO Oxidation Catalysts: Low Temperature CO Oxidation Over Noble-Metal Reducible-Oxide (NMRO) Catalysts," To be Published in the Proceedings of the NASA/RSRE Conference on CO Oxidation Catalysts for Long-Life CO₂ Lasers, NASA Langley Research Center, Hampton, Virginia, October 17-19, 1990.
2. Schryer, D. R., B. T. Upchurch, R. V. Hess, G. M. Wood (NASA Langley Research Center), B. D. Sidney, I. M. Miller (Science and Technology Corporation), K. G. Brown, J. D. Van Norman, J. Schryer, D. R. Brown (Old Dominion Univ.), G. B. Hoflund (Univ. Florida), and R. K. Herz (Univ. California, San Diego), "Pt/SnO₂-Based CO-Oxidation Catalysts for Long-Life Closed-Cycle CO₂ Lasers," To be Published in the Proceedings of the NASA/RSRE Conference on CO Oxidation Catalysts for Long-Life CO₂ Lasers, NASA Langley Research Center, Hampton, Virginia, October 17-19, 1990.

Table 1. Gas Sensor Applications

Application	Material	Reference
CO sensor	Pt/SnO ₂	[81-83]
"	Pt/TiO ₂	[84]
"	Ag/SnO ₂	[85]
"	Au/MgO/SnO ₂	[86]
H ₂ sensor	Pt/Pd/TiO ₂	[87]
"	Ag/SnO ₂ , Pd/SnO ₂	[88]
Combustible gas sensor	Pd/In ₂ O ₃ /SnO ₂	[89]
"	Pd/Sb-doped-SnO ₂	[90]
"	Pd/SnO ₂	[91]
"	Pd/ZnO/SnO ₂	[92]
"	Pd/(SnO ₂ , In ₂ O ₃ , Fe ₂ O ₃ , MnO ₂ , or ZnO)	[93]
Reducing gas sensor	Pt/ZnO	[94,95]
Reducing and oxidizing gas sensor	Pt/SnO ₂	[96]
O ₂ sensor	Pt/ZrO ₂	[97]

Table 2. CO Oxidation Applications

Application	Catalyst	Reference
CO + O ₂ for CO ₂ laser	Pt/SnO ₂	[1,77,98, 99]
"	Pd/SnO ₂	[1,2,100]
"	(Pt or Pd)/Cr/(preferably Mn)/SnO ₂	[101]
"	(Pt and/or Pd)/(optionally Fe, Ru, Cu, or Re)/(Al ₂ O ₃ , TiO ₂ , or MgO)	[102]
"	(Pt, Pd, Rh, or Ir)/(Al ₂ O ₃ or SnO ₂)	[103]
"	Cu/CuO	[99]
CO + O ₂	Pt/CeO ₂ /SnO ₂	[104]
"	Pt/CeO ₂	[19]
"	Pt/TiO ₂	[36,72]
"	Au/(oxide of Fe, Co, or Ni)	[79]
"	Ag/MnO ₂	[9]

Table 3. NO Reduction and Three-Way Automotive Applications

Application	Catalyst	Reference
CO + NO	Pd/SnO ₂	[12]
CO + NO	Pt/V ₂ O ₅ /TiO ₂	[105]
CO + NO & CO + O ₂	(Pt, Pd, Rh, or Ru)/(Mo, W, or V oxide)/TiO ₂	[106]
Three-way automobile catalysts	Pt/Pd/Rh/(various reducible oxides)/Al ₂ O ₃	[107-110]

Table 4. Hydrocarbon Complete Oxidation Applications

Application	Catalyst	Reference
Catalytic heater	Pt/(Sn, Y, or rare-earth)	[111]
"	Pd/Pt/(Ca-aluminate)/SiO ₂ /TiO ₂	[112]

Table 5. Hydrocarbon Partial Oxidation Applications

Application	Catalyst	Reference
Ethylene oxidation	Ag/SnO ₂	[73]
Propylene oxidation	Pd/TiO ₂ , Cu/TiO ₂	[113]
"	Pt/Ba(Sn _{0.6} In _{0.4})O ₃	[114]

Table 6. CO₂ Hydrogenation Applications

Application	Catalyst	Reference
CO ₂ + H ₂ , methane formation	Rh/(Al ₂ O ₃ , MgO, C, ZrO ₂ , TiO ₂ , ZnO, Al ₂ O ₃)	[121]
CO ₂ + H ₂ , unspecified products	Rh/TiO ₂	[122]

Table 7. CO Hydrogenation Applications

Application	Catalyst	Reference
CO + H ₂ , unspecified products	(Rh, Pd, or Ru)/TiO ₂	[74, 123]
"	Rh/TiO ₂	[122,124]
"	Ru/Fe/TiO ₂	[125,126]
"	Ru/(MgO, TiO ₂ , or Al ₂ O ₃ /TiO ₂)	[35]
"	Rh/TiO ₂	[53,54]
"	Pt/TiO ₂	[127]
CO + H ₂ , methane formation,	Pt/(TiO ₂ or Nb ₂ O ₅)	[42]
"	Pt/TiO ₂	[10,43]
"	(Rh, Ir, Ru)/TiO ₂	[128]
CO + H ₂ , olefin synthesis	Ru/TiO ₂	[129]
CO + H ₂ , Fischer-Tropsch synthesis	Ru/Fe/TiO ₂ , Fe/TiO ₂	[13]
"	Co/Re/TiO ₂	[130]
"	Co/Ru/TiO ₂	[131]
"	Ru/(Nb, Ta, or V oxide)/TiO ₂	[132]
CO + H ₂ , liquid-phase reaction	Ru/(TiO ₂ or Nb ₂ O ₅)	[133]

Table 8. Alcohol Synthesis, Methanol Decomposition Applications

Application	Catalyst	Reference
CO + H ₂ , methanol synthesis	Cu/ZrO ₂	[134,135]
"	Cu/ZnO	[28,29,136, 137,158]
"	(Pt, Rh, or Ir)/(MgO or ZnO)	[11]
"	Pd/(TiO ₂ or Nd ₂ O ₃)	[138]
CO + H ₂ , CH ₄ and methanol synthesis	Pd/(TiO ₂ or SiO ₂)	[55]
CO + H ₂ , alcohol (ethanol) synthesis	La ₂ O ₃ -promoted-(Rh or Rh/Pt)/TiO ₂	[139]
Methanol decomposition to CO + H ₂	Ni/SiO ₂ /MgO	[33]

Table 9. Hydrocarbon Reforming and Related Applications

Application	Catalyst	Reference
Reforming	Pt/Sn/Al ₂ O ₃	[48,140]
"	Pt/Ni-sulfide/SnO ₂	[141]
Hydrogenolysis of alkanes	Ru/(various metal oxides)	[25]
Isomerization	Pt/S-containing-halide/ZrO ₂	[142,143]
Paraffin isomerization	Pt/Rh/halide/SnO ₂	[144]
Dehydrogenation	Pt/ZnO/SnO ₂	[145]
"	Pt/Li/GeOx/SnO ₂	[146]
Dehydrocyclization	Pt/Co/SnO ₂ /Al ₂ O ₃	[147]
Hydroprocessing of aromatics to cyclo-paraffins	Pt/Co/Cl/SnO ₂	[148]

Table 10. Electrochemical and Photochemical Applications

Application	Catalyst	Reference
Methanol electro-oxidation	(Pt or Pd)/SnO ₂	[37,38,39]
Fuel cell (air electrode)	Pt/SnO ₂	[39,149,150,151]
"	Pt/Sb-promoted-SnO ₂	[56,152]
O ₂ & Cl ₂ evolution	(Pt, Pd, or Ru)/SnO ₂	[153]
Photocatalytic lignin oxidation	(Pt, Ag, or Au)/TiO ₂	[154]
Electrosynthesis of peroxides	Pt/Sb ₂ O ₅ /SnO ₂	[155]
Photoassisted H ₂ production	CdS/SiO ₂ plus Pt/(TiO ₂ , ZnO, SnO ₂ , or WO ₃)	[156]
Photography	Ag/Pd/TiO ₂	[157]

Table 11. Miscellaneous Applications

Application	Catalyst	Reference
Vinyl acetate production	Pd/Au/SnO ₂	[115]
Alcohol oxycarbonylation	Pd/V ₂ O ₅ /TiO ₂	[116]
CO + H ₂ O, light olefin synthesis	Rh/Nb ₂ O ₅	[117]
CO + H ₂ O, water gas shift	Cu/ZnO	[118]
Electroless deposition of Pd/SnO _x for electroplating	Pd/SnO _x	[119]
CO chemisorption	Os/TiO ₂	[120]
Unknown reaction	Rh/Au/(SiO ₂ , TiO ₂ , or Al ₂ O ₃)	[26]

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